

Mechanism of Self-Diffusion in Diamond

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It is shown via state-of-the-art theoretical calculations that self-diffusion in diamond is dominated by vacancies, independent of the position of the Fermi level. This is very different from self-diffusion in silicon and germanium, where vacancies, interstitials, and direct-exchange mechanisms all have comparable activation energies. The dominance of the vacancy mechanism is due to the stiffness of diamond bonds, which precludes bond twisting and large relaxations, and to the high electronic density and the large band gap in diamond, which result in a strongly repulsive potential-energy surface for self-interstitials.

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Diamond has the potential of becoming an important special-purpose electronic material because of its tolerance of a high-temperature environment and its high electron and hole mobilities. The interest in diamond has increased substantially with the development of techniques for the deposition of thin diamond films. To date, several groups have succeeded in growing large-surface-area films consisting of small diamond microcrystallites.¹ The growth of a single-crystal film on a nondiamond substrate, however, has proven much more difficult and has not yet been achieved despite substantial efforts by many research groups. Since the growth of the film proceeds simultaneously at many nucleation centers, the development of a continuous, single-crystal film must necessarily involve atomic motion of both surface and subsurface atoms. The determination of the mechanisms of atomic motion in the bulk is, therefore, an important step in the effort to understand and improve the methods of growth of diamond thin films.

The general problem of diffusion and self-diffusion in semiconductors has recently attracted significant theoretical²⁻⁵ and experimental^{6,7} attention as a result of the development of accurate theoretical techniques and new experimental methods. The determination of diffusion mechanisms is not easy, however, since diffusion can proceed along many paths. Even in the simpler case of self-diffusion (diffusion of native tracer atoms) several elementary diffusion mechanisms need to be considered. In Si, for example, it has been found that diffusion mechanisms involving vacancies, interstitials,^{2,3,7,8} and direct exchange of atoms in a Si lattice⁵ have comparable activation energies and all contribute to self-diffusion. The activation energy for self-diffusion has been measured in Si,⁹ as well as the formation⁷ and migration¹⁰ energies of the vacancy. However, the dominant diffusion mechanisms may be quite different in diamond, since the bonding characteristics in carbon structures are significantly different from those in silicon and germanium; i.e., carbon atoms readily form multiple bonds, while

Si and Ge do not. This manifests itself both in the existence of two competing structures for solid carbon, namely graphite and diamond, as well as in the structures of carbon clusters¹¹⁻¹³ being totally different from those of Si and Ge.¹⁴⁻¹⁶ Other differences between diamond and Si are the much greater electron density in diamond (r_s values of 1.3 and 2.0 a.u. for diamond and Si, respectively) as well as a much larger bulk modulus of diamond, resulting in a lower propensity for reconstruction. These differences may result in distinct reconstruction patterns and significantly altered energetics for point defects, saddle-point configurations for diffusion, and different charge-state behavior. To date, no experimental data regarding self-diffusion in diamond have been reported. Early theoretical calculations for diamond used semiempirical methods to extract the formation¹⁷ and migration^{17,18} energies of the vacancy and the interstitial,¹⁹ but results obtained by these techniques have substantially disagreed with the more recent results of *ab initio* calculations^{2,3,20} (see also Refs. 21 and 22).

Local density calculations for bulk diamond²³ have successfully reproduced the structural properties of diamond (see Table I). These calculations used nonlocal pseudopotentials²⁴ and the plane-wave method. The present calculations²⁵ have also used the plane-wave method, and a softer pseudopotential of the Hamann-Schluter-Chiang-type generated by enlarging the pseudopotential matching radius.²⁶ This potential has good

TABLE I. Comparison of calculated structural properties of diamond with experiment.

	a (Å)	B_0 (Mbar)	B'_0	E_{coh} (eV/atom)
This work ^a	3.62	4.38	3.5	7.9
Ref. 20 ^b	3.56	5.03	3.6	7.7
Expt. ^c	3.567	4.43	4.0	7.37

^a $E_1 = 14.2$ Ry; $E_2 = 25.8$ Ry.

^c As quoted in Ref. 23.

^b $E_1 = 60$ Ry.

accuracy (see Table I) while allowing for large-scale calculations. After extensive convergence tests with and without the use of Löwdin's perturbation theory, we have settled on a 14.2-Ry cutoff for the plane waves included directly, and a 25.8-Ry cutoff for the waves included via perturbation theory. For comparison, Ref. 23 included plane waves up to 60 Ry directly, while a total-energy calculation for SiC (Ref. 27) used 24 and 48 Ry as the direct and Löwdin cutoffs, respectively. The calculations were carried out in supercell geometry, with supercell size corresponding to sixteen atoms in the perfect crystal. For the vacancy, which turned out to be the lowest-energy defect, the calculations were repeated with a 32-atom supercell. The change in the vacancy formation energy was 0.3 eV. The convergence of the key results was also checked with use of cutoffs of 21 and 42 Ry, respectively. The changes in the calculated total-energy differences were less than 3%.

The contribution of a particular defect to the self-diffusion coefficient is given by

$$D = D_0 \exp[-(E_F + E_M)/kT], \quad (1)$$

where E_F and E_M are the defect formation and migration energies, respectively. For the direct exchange, the activation energy is equal to the saddle-point energy. In the search for the lowest-energy diffusion paths, we have carried out calculations for the vacancy, for various configurations of the interstitial, and for the saddle point for the direct exchange in diamond (see Fig. 1 and Table II). The tabulated results include the energy gains upon a symmetric relaxation of the nearest-neighbor atoms and an estimate of the longer-range relaxations using Keating's valence force field.²⁸

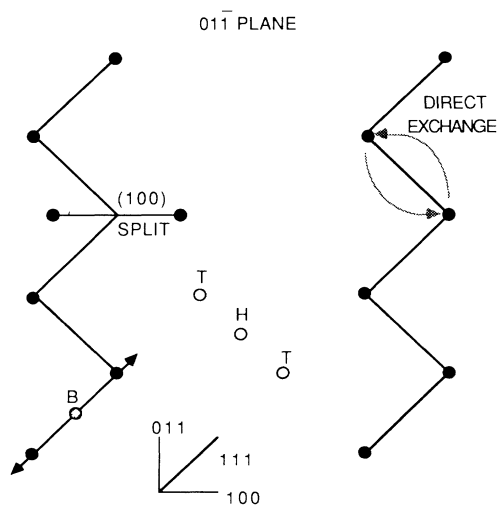


FIG. 1. Schematic view of the native defect and direct-exchange configurations which can be involved in self-diffusion in a diamond lattice. T, H, and B denote the tetrahedral, hexagonal, and bond-centered sites. Several of the interstitial configurations are accompanied by significant lattice relaxations. See text.

Since it is known that the Si vacancy distorts tetragonally due to the Jahn-Teller effect, we have included these effects in our calculations. For the neutral vacancy, the tetragonal distortion lowered its energy by 0.25 eV (included in Table II). Its formation energy is 7.2 eV, making it the lowest-energy elementary defect. The radial outward relaxation of its nearest neighbors was only about 5% of the bond distance and the total energy gain was 0.3 eV. This result shows that the extreme hardness of diamond strongly dominates over the tendency of carbon atoms to go planar when threefold coordinated.

The tetrahedral interstitial has a formation energy of 24 eV compared to 4–5 eV in Si. The radial relaxation of the nearest neighbors is minimal (1%) and the concomitant lowering of the total energy is negligible. The very large formation energy of the interstitial in diamond can be explained by the large band gap and the high electron density in diamond, compared to Si (r_s of 1.3 and 2.0 a.u., respectively). The additional electrons of the tetrahedral interstitial have high kinetic energy, resulting in a large formation energy. Stated somewhat differently, the T_2 level of the tetrahedral interstitial, which is occupied by two electrons in its neutral charge state, lies very close to the bottom of the conduction bands, and the band gap in diamond is large. The formation energy of the doubly positively charged interstitial, however, is still large (15.2 eV with the Fermi energy at the top of the valence bands). Another reason for the large formation energy of interstitials in diamond is the absence of d orbitals in the vicinity of the occupied states. Tests in Si have shown that the elimination of the d orbitals from the basis set in an LCAO calculation raises interstitial formation energies significantly.

For the split and bond-centered interstitials, the relaxation of the surrounding lattice and the resulting relaxation energies are larger. For example, the nearest neighbors relax radially by 15% and 20% for the cases of split $\langle 100 \rangle$ and bond-centered interstitials, respectively. The formation of energies, however, have remained large (16.7 and 15.8 eV), so that the bond-centered and split interstitials are unlikely to contribute to self-diffusion.

The remaining simple mechanism for self-diffusion is that of direct exchange, in which two atoms on lattice sites exchange positions. Pandey⁵ has studied this process extensively in Si. In particular, he identified the energetically most favorable path for the direct exchange and labeled it "concerted exchange." In this path, the

TABLE II. Calculated formation energies of elemental point defects and the saddle-point energy for the direct exchange in diamond (eV).

	Tetrahedral interstitial	$\langle 100 \rangle$ split interstitial	Bond-centered interstitial	Direct exchange
Vacancy	7.2	23.6	16.7	15.8
				13.2

atoms rotate around the bond center in such a way that only two bonds remain broken at any one time. The calculated energy of the saddle point in this concerted-exchange configuration is 13.2 eV.

It is clear from the results presented above that the dominant mechanism for self-diffusion in diamond is the vacancy diffusion. Self-diffusion in diamond is thus very different from that in Si, where vacancies, interstitials, and direct-exchange mechanisms all contribute. We have calculated the activation energies for the various self-diffusion mechanisms in the remaining group-IV semiconductor, germanium, and found them very similar to the ones reported for Si.

Since the vacancy is the dominant diffusing species, we have calculated the variation of its formation energy in the T_d symmetry as a function of Fermi-level position in the gap. The equilibrium charge state of the vacancy for a given Fermi-level position is of course determined by its formation energy. The results, plotted in Fig. 2, show that the electronic U is larger in diamond than in Si (0.6 vs 0.2 eV), as expected. The Jahn-Teller distortions from tetrahedral symmetry result in energy gains of 0.25 and 0.05 eV for the neutral and positively charged states, respectively. With use of approximate formulas for multiplet effects,²⁹ the vacancy in diamond will not be a negative- U center if the multiplet splitting is smaller than 0.6 eV. Scaling of the results for Si suggests a multiplet splitting of 0.5 eV in diamond.²⁹

Experimentally, absorption and luminescence spectra labeled GR1 have been assigned to the neutral vacancy in radiation damaged diamond,³⁰ although ideally an EPR spectrum would be needed for positive identification. The assignments to the neutral charge state is partially based on the observation that all acceptors in p -type diamond have to be compensated before this spectrum is seen.³¹ Both ours and previous²⁰ calculations show that the vacancy is indeed ionized in p -type dia-

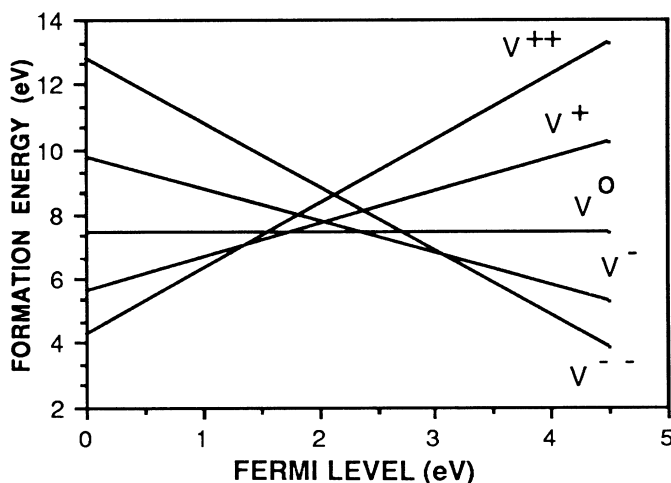


FIG. 2. Formation energy of the various charge states of the T_d -symmetric vacancy as a function of the Fermi-level position.

mond. An estimate of the Jahn-Teller energy of the GR1 center, based on a fit to its luminescence spectrum and certain assumptions about the restoring forces, gives about 100 meV (Ref. 32).

The large band gap of diamond allows for the existence of several charge states of the vacancy. Although it is difficult at present to assess the accuracy of local density calculations for highly charged defect states, the results show that a highly positively (negatively) charged vacancy has a significantly lower formation energy than a neutral vacancy at lower (higher) Fermi-level positions. Since the calculated migration energies are almost charge independent (see below), one may draw the conclusion that self-diffusion will be Fermi-level dependent, and, in particular, be enhanced in both p - and n -type diamond, as a result of the lowering of the activation barrier for charged vacancy diffusion.

Although the formation energy dominates the activation energy for diffusion, the migration-energy contribution is sizable for diamond. By symmetry, the reaction coordinate for vacancy diffusion is the line connecting a nearest-neighbor atom with the vacancy, the saddle point being at the midpoint. The energy of the saddle point lies 1.7–1.9 eV above the equilibrium vacancy configuration, depending on the charge state of the vacancy. This number includes 1.2-eV energy gain due to the radial relaxation of the neighboring atoms. In radiation damage experiments, the GR1 center was found to be mobile above 800°C (Ref. 33). Above this temperature it is trapped by nitrogen and subsequently enhances its motion.³³ For comparison, the activation energy for N diffusion in diamond is also high³⁴ (2.6 eV).

The above results suggest that the motion of extended defects, such as grain boundaries and dislocations, is assisted by vacancies, but not by interstitials and direct-exchange mechanisms. Furthermore, the activation energy for self-diffusion in diamond is high, e.g., 9.1 eV for the neutral vacancy. Since the motion of extended defects, such as grain boundaries, is assisted by point-defect diffusion, the high activation barrier for self-diffusion impedes their motion and is probably the reason for the lack of annealing of grain boundaries in thin-film diamond, despite relatively high growth temperature in most methods of preparation. However, as pointed out above, diamond growth under p - or n -type conditions may lower the diffusion barrier and thereby allow for better annealing of defect structures.

The early work on defects in diamond used simple models¹⁷ or semiempirical Hamiltonians.^{18,19} Our results suggest that, in that early work, the formation energy of the vacancy was substantially underestimated¹⁷ (as was also the case for Si), while the migration energy^{17,18} was relatively close to our value. For the interstitial, the variation in formation energy between the tetrahedral and bond-centered sites is much smaller than that found by the previous workers.¹⁹

The present predictions can be tested. For example,

radioactive tracer experiments can measure activation energy for self-diffusion,⁹ which would then be compared with our prediction of 9.1 eV. The same experiment could be repeated in *p*- and *n*-type diamond to check the prediction that the self-diffusion activation energy is lowered. In addition, the migration energy of the GR1 center could be measured. An agreement between the measured value and the one calculated for the vacancy would further strengthen the identification of the GR1 center as a vacancy. Finally, the growth of either *p*- or *n*-type diamond would provide a test of the prediction that the reduced self-diffusion activation energy should lead to a better quality material.

In summary, we have examined self-diffusion processes in diamond and shown that they are dominated by the vacancy mechanism independently of the position of the Fermi level. The reasons for the dominance of the vacancy mechanism are (i) the stiffness of the carbon bonds, which prevents twisting of the bonds (occurring during direct exchange) as well as large relaxations around defects or saddle points for migration; and (ii) the large band gap and the high electron density in diamond, which results in a highly repulsive potential-energy surface for interstitial configurations. Self-diffusion in diamond, however, is considerably different from self-diffusion in silicon or germanium, in which vacancies, interstitials, and direct exchange mechanisms all contribute.

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Note added.—Since the submission of this manuscript the migration energy of the GR1 center has been measured by Davies and Lawson.³⁵ The experimental value of 1.9 eV agrees very well with the theoretical one (also 1.9 eV), which lends additional support for the identification of the GR1 center as a vacancy. We would like to thank G. Davies and S. Lawson for allowing us to quote their results prior to publication.

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